

**Voltammetric, Spectroelectrochemical and Electrical Characterization of Poly-transition metals-tetraaminophthalocyanine-modified electrodes: Electrocatalytic reduction of CO<sub>2</sub>**

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Electrochemical reduction of CO<sub>2</sub> is an important target in environmental chemistry. It has been studied on metallic and semiconductor electrodes, with relative success (1), but these surfaces need large overpotentials to reduce the molecule of carbon dioxide. To solve this point, macrocyclic complexes adsorbed on carbon surfaces have been studied. In this work we shown the electrochemical reduction of CO<sub>2</sub> catalyzed by poly-tetraaminophthalocyanines of transition metals (Fe, Co, Ni, Cu) and by the metal free (H<sub>2</sub>) polymerized ligand adsorbed on glassy carbon electrodes. Co, Ni, Cu, and H<sub>2</sub> macrocycles were electropolymerized from a 0.1 M tetrabutyl ammonium perchlorate/DMF solution containing 10<sup>-3</sup> M of the complexes, by continuously cycling the potential during 50 cycles in a potential range of 0.6 up to 1.0 V vs. Ag/AgCl. For the iron macrocycle the solvent used was DMSO. Voltammetric studies: The modified electrodes, in a 0.1 M NaClO<sub>4</sub> solution under N<sub>2</sub> atmosphere show redox processes that can be attributed to the ligand or to the metal center. When the solution is saturated with CO<sub>2</sub> an increment in the cathodic current is observed for all the polymers. This increment is due to the electroreduction of CO<sub>2</sub>. The more active polymer- modified electrode is the cobalt one (less potential to begin the reaction). The potential of the reduction of CO<sub>2</sub> in this case is close to 0.8 V vs. Ag/AgCl. The decreasing order in electrocatalytic activity for the other polymers is: Ni > Cu > Fe > H<sub>2</sub>. Spectroelectrochemical studies: Polymers grown on a conducting glass electrode can be studied by spectroelectrochemical techniques. In this way, the spectra of the modified electrodes were recorded at open circuit potential and at potentials where the reaction takes place. At open circuit potentials only two bands can be observed. They correspond to the Soret and Q bands, both assigned to p-p\* transitions. At open circuit potentials, the behavior in N<sub>2</sub> or CO<sub>2</sub> is very similar. At negative potentials corresponding to the foot of the reduction wave, the spectra change dramatically from N<sub>2</sub> to CO<sub>2</sub>. In N<sub>2</sub> a charge transfer band (metal (I) to ligand) appears between the Soret and Q bands (2). In CO<sub>2</sub> atmosphere this band disappears showing that metal (I) is oxidized by CO<sub>2</sub>. However, the potential where the metal is reduced to metal (I) does not correspond to the potential where the reduction of CO<sub>2</sub> begins. This fact can be explained in terms of a coop-

erative effect between the metal in the oxidation state of (I) and the reduced ligand. This explanation agrees with the negligible activity of the metal free polymer modified electrode. Electrochemical Impedance Spectroscopic (EIS) studies: Conducting polymers are frequently analyzed for EIS, because this technique permits to get information about the electrical behavior, double layer characteristics, and charge transfer aspects. One of the facts that can be observed is that the metals can modify the morphology of each polymer. In this sense, the low-frequency capacitance C<sub>lf</sub> values changes according the metallic center. For example, the Cu-polymer modified electrode has a value of 879 mF/cm<sup>2</sup> while the Co-modified electrode has a value of 140 mF/cm<sup>2</sup>. On the other hand, when CO<sub>2</sub> is present in the solution, the spectra taken at potentials where the reduction takes place, it can be observed a decreasing of one order of magnitude in the C<sub>lf</sub> values for all the polymers except the metal free one. The above description could be indicates that the presence of CO<sub>2</sub> changes the morphology of the polymers and the characteristics of the double layers. The products of the reaction are different for each polymer-modified electrode. For example, Fe-polymer modified electrode shows an interesting selectivity to formaldehyde. Other products of the reaction detected are CO and H<sub>2</sub>. References 1.F.R.Keen, *Electrochemical and Electrocatalytical reactions of carbon dioxide* B.P. Sullivan, K. Krist, H.E. Guard Eds.Ch 1, Elsevier Sci. Pub. Netherlands. 2.E.Trollund P.Ardiles, M.J.Aguirre, S.R.Biaggio, R.C.Rocha-Filho, *Polyhedron*, 19, (2000),2303 Acknowledgements This work has been supported by Fondecyt projects 1980837, 2000010, 1000746 and Dicyt-USACH. F.A grateful to a Conicyt Doctoral Scholarship.